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(54) Thickened Film-forming Compound

(57) The invention concerns a thickened film-forming compound comprised of a film-forming polymer and a polysaccharide alkyl ether for the thickener that is composed of designs with at least two different osidic cycles, with each design having at least one hydroxyl group substituted with a saturated hydrocarbon alkyl chain.

The polysaccharide alkyl ether preferably has a molecular weight higher than 200,000 and is specifically an alkyl ether of guar gum having a degree of substitution of around 2 to 3, in particular 2.5.

The compound obtained can be used especially in the cosmetic fields of keratinic materials and is designed more especially for the treatment and care of the nails.

**Thickened composition containing a film-forming polymer-EP 0898958A1**  
(Translation)

This invention referred to a thickened composition containing a film-forming polymer and an alkyl-ether polysaccharide formed from units comprising at least two different osidic rings, each unit having at least one hydroxyl group substituted by a saturated alkyl hydrocarbon chain, as a thickener.

Preferably, the alkyl-ether polysaccharide has a  $M_w$  greater than 200,000, and it is quoted alkyl-ether guar gum having a degree of substitution of 2 to 3, particularly 2.5.

This composition can be further processed in a cosmetic end-product that can apply to a keratin based substrate, and it targets particularly a nail care treatment.

**Description**

[0001] This invention has as objective obtaining of a film-forming compound, composed of film-forming polymer and a new cosmetic thickener. The invention also includes utilization of the above mentioned composition to formulate cosmetic products that can apply to keratin based substrates like: skin, nails, eye lash, eye brown, hair or mucous membrane such as lip or inside the eye lid. It is particularly dedicated to a nail care product.

[0002] More precise, the invention refers to a composition containing film-forming polymers that can form a homogeneous and continuos film on a substrate such as nail, eye brown, hair.

[0003] In this film-forming composition such as nail polish, the organic phase has been thickened by a thickening agent.

[0004] Clays are well known as thickeners, example organomodified gypsum that is described in GB-A-2021411. Preparation of such a composition needs a good dispersion of the clay in the mixture. To prepare a suspension like the one mentioned, it is necessary to use a Gaulin high pressure homogenizer, in a separate stage during the manufacturing process. This long and complicate stage can be avoided if a thickening agent is used. In addition, by adding clays (like organomodified gypsum) can modify the properties of the obtained film. As a result this film is less resistant to mechanic shocks and it dries easier.

[0005] Hydrophilic and hydrophobic silica is well known as thickener, and this was mentioned in FR-A-1453089. Sometimes, silica needs to be predispersed in base in a separate stage, during the process. In addition, silica has the tendency to create opaque products. This should be avoided when preparing a transparent film-forming composition that can lead to a shining film it is in place.

[0006] At the beginning of the present invention it is proposed a transparent thickened film-forming composition, that can apply to nail care products, and it presents good cosmetic properties without having the above mentioned disadvantages.

[0007] This discovered composition can be obtained using a particular thickener.

[0008] The objective of the present invention is to prepare a composition comprising a film-forming polymer and an organic phase, and which also contains an alkyl-ether polysaccharide formed from units comprising at least two different osidic rings, each unit having at least one hydroxyl group substituted by a saturated alkyl hydrocarbon chain, provided that the organic phase contains at least one solvent for the alkyl-ether polysaccharide.

[0009] Due to presence of the alkyl-ether polysaccharide the above mentioned composition has a transparent appearance and the desired viscosity. This thickener applies perfectly to a stable pigmented composition such as nail polish.

[0010] By "alkyl hydrocarbon chain" it is understood a linear or branched hydrocarbon chain composed of 1 to 24 carbon atoms, preferred 1 to 10, better 1 to 6, but the most preferred 1 to 3 carbon atoms. Particularly, this alkyl chain is a saturated alkyl chain and it is especially selected from Me, Et, n-Pr, i-Pr, n-Bu, i-Bu, t-Bu. Manufacture of the alkyl-ether polysaccharide has been described in EP-A-281360, EP-A-708114, EP-A-281360.

[0011] Preferably,  $M_w$  of the alkyl-ether polysaccharide needs to be greater than 100,000 but especially greater than 200,000, and it can go up to 1million. This alkyl-ether polysaccharide can have 1 to 6 hydroxyl groups, preferred 2 to 4 hydroxyl groups that are substituted by a saturated or nonsaturated alkyl hydrocarbon chain.

[0012] Osidic groups are preferably selected from mannose, galactose, furanose, rhamnose and arabinose.

[0013] As a preferred method to achieve the composition, this alkyl-ether polysaccharide is a alkyl-ether of a gum, particularly a overall nonionic gum, on other words behaving less or non ionic. As an appropriate gum it can be named guar gum due to the fact that contains galactose and mannose, karaya gum that is a mixture of rhamnose, galactose and acid galacturic, tracangath gum that is a mixture of arabinose, galactose and acid galactouric.

[0014] As a preferred method, alkyl-ether polysaccharide is a derivative of guar gum. Also, the more advantageous alkyl-ether polysaccharide is a alkyl galactomannan, with alkyl chain of  $C_1$  to  $C_6$ , preferably,  $C_1$  to  $C_3$ , and especially ethyl guar with a degree of substitution of 2 to 3, preferably about 2.5 to 2.8, such as the one described by documents RD 95378007 (October 1995) and EP-A-708114. This particular gum is commercialized by Aqualon under the name of N-HANCE AG 200®, and N-Hance AG50®.

[0015] Concentration of alkyl-ether polysaccharide depends upon galenic form of the end-product, and upon quantity of organic phase to be thickened. Particularly, the weight ratio of the amount of liquid oil phase to thickener is 5 to 500. For example, alkyl-ether polysaccharide concentration (by weight) can go from 0.2 to 20%, preferred from 1.5 to 8%.

[0016] According to the invention, the solvent for the alkyl-ether polysaccharide can be an organic solvent or an oil. In other words alkyl-ether polysaccharide is a thickener for the organic solvent and the oil. By oil it is understood all fatty materials that are liquids at room temperature.

[0017] For example, an organic solvent can be one of the following:

- Liquid ketones (at room temperature) such as methyl ethyl ketone, diisobutyl ketone, isophorone, cyclohexanone, acetone.
- Liquid alcohols (at room temperature) such as ethanol, isopropanol, diacetone alcohol, 2-butoxyethanol, cyclohexanol.
- Liquid glycols (at room temperature) such as ethylene glycol, mono n-butyl ether of propylene glycol.
- Esters with a short chain (going from 3 to 8 carbon atoms) such as ethyl acetate, methyl acetate, propyl acetate, n-butyl acetate, isopentyl acetate.
- Liquid esters (at room temperature) such as diethyl ether, dimethyl ether, or dichlorodiethyl ether.
- Liquid alkanes (at room temperature), such as decane, heptane, dodecane, cyclohexane.
- Liquid aromatic compounds (at room temperature), such as toluene and xylene.
- Liquid aldehydes (at room temperature) such as benzaldehyde, acetaldehyde.

[0018] These solvents are the most convenient particularly for make-up products or nail care products: the composition includes nail polish as well as nail care products.

[0019] Oils that can be used as solvents for the alkyl-ether polysaccharide are listed below:

- Vegetable oils as liquid triglycerides such as corn oil, soybean oil, jojoba oil, pumpkin oil, raisin seed oil, sesame oil, hazelnut oil, apricot oil, macadamia oil, castor oil, triglyceride derived from acid caprylic/capric, such those manufactured by STEARINES DUBOIS, or DYNAMIT NOBEL under the name of MIGLYOL 810, 812 and 818.
- Animal oils such as lanolin.
- Mineral oils.
- Synthetic oils like fatty alcohols, such as ester of octyl-2-dodecanol, and particularly, fatty acids esters, especially with a total number of carbon atoms of 12 to 80, preferably between 16 to 50; silicone phenylate, preferably phenyl trimethicone, diphenyl dimethicone, polymethyl phenyl siloxane.

[0020] Any other product that art people can prove as being a solvent for a alkyl-ether polysaccharide, using a simple method.

[0021] These oils are convenient solvents for the alkyl-ether polysaccharide particularly for preparing of a nail care product.

[0022] Complementary oils nonsolvents for alkyl ether polysaccharide can also help the composition. As complementary oils can be mentioned: resins, silicone liquid (at room temperature) gums, partially fluoride hydrocarbon oils, perfluoride oils, silicone oils exempt those containing aromatic groups, example linear or branched polysiloxane, such as polydimethyl polysiloxane, polyethylmethyl polysiloxane, polyalkylmethylsiloxane; and cyclic polysiloxane such as octamethylcyclotetrasiloxane, decamethylcyclopentasiloxane, or a mixture thereof; fluoride hydrocarbon oils polysiloxane functionalized by one or more hydroxyl groups and/or by many polyether groups such as dimethicone copolyols; linear or branched hydrocarbons such as petrolatum, i-hexadecane, i-dodecane.

[0023] Concentration of the alkyl-ether polysaccharide's solvent (organic solvent or oil) can go from 40 to 99.3% from total organic phase composition, preferred 72 to 98.5%. Complementary oils can be added to the composition. Their concentration is 0 to 75%, from the total organic phase composition, preferred 0 to 50%.

[0024] The film-former polymer introduced by this invention can be a polymer commonly used in nail polish products, and an appropriate solvent well known by art people. Example of the polymers: nitrocellulose, cellulose acetobutyrate, alkyde resin, resins resulting from condensation of formaldehyde and arylsulfonamide, polyesters, polyuretanes, polyesters-polyuretanes, polyether-polyuretanes, polymers radicals particularly acrylic, styrene-acrylic and/or vinyl and a mixture thereof.

[0025] These polymers can be dissolved or dispersed in the composition. Generally, concentration of the polymer is 0.5 to 40% from the total composition, preferred 10 to 20%.

[0026] Due to the presence of alkyl-ether polysaccharide, it is possible to use pyrogenic silica which can help considerable the viscosity of the composition, without compromising the brilliance of the film.

[0027] Pyrogenic silica can be a hydrophobic or a hydrophilic pyrogenic silica.

[0028] These pyrogenic silica can be obtained by hydrolysis of a volatile compound at elevated temperature, in a oxyhyric flame, resulting a fine powder of silica. This procedure allowed especially to obtain hydrophilic silicas with many silanol groups on the surface. Examples of these hydrophilic silicas: AEROSIL 130®, AEROSIL 200®, AEROSIL 255®, AEROSIL 300®, AEROSIL 380®, by DEGUSSA, or CAB-O-SIL HS5®, CAB-O-SIL EH-5®, CAB-O-SIL LM-130®, CAB-O-SIL MS-55®, CAB-O-SIL M-5®, by CABOT.

[0029] It is possible to chemically modify the surface of the above mentioned silica, by a chemical reaction that can generate a lower number of silanol groups. A notable number of silanol groups can be substituted by hydrophobic groups, resulting a hydrophobic silica.

[0030] Hydrophobic groups can be as follows:

- Trimethylsiloxyl groups, particularly obtained by treatment of pyrogenic silica in the presence of hexamethyldisilazane. These silicas are named "silica silylate" by CTFA (6<sup>th</sup> edition 1995). They are commercialized under the name of AEROSIL R812® by DEGUSSA, or CAB-O-SIL TS-530®, by CABOT.
- Dimethylsiloxyl or polydimethylsiloxane groups, particularly obtained by treatment of pyrogenic silica in the presence of polydimethylsiloxa, or dimethyldichlorosilane. These silicas are named "silica dimethylsilylate" by CTFA (6<sup>th</sup> edition 1995). They are commercialized under the name of AEROSIL R972®, AEROSIL R974® by DEGUSSA, or CAB-O-SIL TS-610®, CAB-O-SIL TS-720® by CABOT.

[0031] Preferred size of the pyrogenic silica can go from nanometer to micrometer, average about 5 to 200 nm.

[0032] Concentration of the pyrogenic silica described in this composition can go from 0.1 to 5% from the total organic phase composition, preferably 0.1 to 1%.

[0033] Due to the presence of alkyl-ether polysaccharide, it is also possible to add a clay to the composition, such as organomodified bentonite, without interfere with the properties of the film. Concentration of the clay is between 0.1 to 3%, from the total composition, preferably 0.5 to 1.5%. They are commercialized under the name of BENTONE 27®, BENTONE 34®, BENTONE 38®, by RHEOX, or TIXOGEL LG®, by SUD CHEMIE.

[0034] Beside the film-forming polymer, the composition can also include a plasticizer, which helps the flexibility of the film without weaken its physical resistance.

[0035] These plasticizers are those already confirmed to be used in nail polish products. As plasticizers can be named the following: dibutyl phthalate, diisobutyl dioctyle phthalate, dimethoxyethyl phthalate, benzyl benzoate, glyceryl phthalate, triethyl citrate, tributyl phthalate, acetyl citrate, phosphate, triphenyl, glycol, camphre, along with their derivative or a mixture thereof. Concentration of plasticizers can go between 1 to 30% from the total composition, preferred 5 to 10%.

[0036] In this document were included adjuvants commonly used in cosmetic. It can be listed: colorants, pigments, lacks, anti-UV agents, thickening agents, surface active agents, waxes, perfumes, or active ingredients such as: D-panthenol, phytantriol, vitamins and their derivatives, keratin and its derivatives, melanin, collagen, cystine, chitosan and its derivatives, biotin, trace elements, glycerin, phospholipids, moisturizing agents. Of course, art people will want to choose any particular adjuvant and/or its concentration, as long as it does not alter the above-described composition.

[0037] This composition can be used in: make-up products, cosmetic treatment products, or care of the keratin based substrate and/or mucous membrane products, depend upon the active ingredients being use. As make-up products can be listed: nail polish, eye-liner, mascara, concealer, foundation.

[0038] However, this composition is used especially for nail polish and nail care products. As an objective this inventions refers to a nail polish or nail care product, comprising a film-forming polymer, an organic phase, and an alkyl-ether polysaccharide that was previously described.

[0039] The invention equally refers to a cosmetic treatment or make-up applied to keratin based substrate and/or mucous membrane as those previously described.

[0040] The invention equally refers to a cosmetic treatment or make-up applied to keratin based substrate, especially nail and/or mucous membrane, consisting in applying of the above mention composition to the tissues.

[0041] The following examples are given to illustrate embodiments of the invention, and there are not intended to limit the scope of the invention otherwise described herein.

#### **Example1:**

A nail polish was prepared having the following composition:

- Film-forming polymer (nitrocellulose, resin) 28g
  - Plasticizer 7g
  - IPA 5g
  - Ethyl guar with a degree of substitution about 2.5 (1) 3g
  - Pigment 1g
  - Ethyl acetate/butyl acetate qsp
- (1) commercialized under the name of N-HANCE AG 200® by AQUALON

[0043] Apply this product on nails. After drying it is obtained a smooth, homogeneous and shining film.

#### Example 2:

[0044] A nail care product was prepared having the following composition:

- film-forming polymer (nitrocellulose, resin) 14g
  - plasticizer 3g
  - UV filter 0.5g
  - Pigments 0.1g
  - Pyrogenic silica (Degussa 200) 0.5g
  - IPA 5g
  - Ethyl guar with a degree of substitution about 2.5 (1) 0.5g
  - D-panthenol 0.5g
  - Phytantriol 0.1g
  - Butyl acetate/ethyl acetate qsp
- (1) commercialized under the name of N-HANCE AG 200® by AQUALON

[0045] Apply this product on nails. After drying it is obtained a homogeneous and shining film that improve the appearance of the nail.

#### Example 3:

[0046] ] An oil nail care product was prepared having the following composition:

- acetobutyrate cellulose 0.5g
  - mineral oil 5g
  - pyrogenic silica (degussa 200) 0.5g
  - Ethyl guar with a degree of substitution about 2.5 (1) 0.5g
  - Additives (actives and pigments) 1g
  - IPA 5g
  - Propylene glycol monomethyl ether 3g
  - Volatile silicon oil 20g
  - Vegetable oil qsp
- (1) commercialized under the name of N-HANCE AG 200® by AQUALON

[0047] This product can be easily applied to the nails and massaged in the matrix of the nail.

## Claims

1. Composition comprising a film-forming polymer and an organic phase, and which also contains an alkyl-ether polysaccharide formed from units comprising at least two different osidic rings, each unit having at least one hydroxyl group substituted by a saturated alkyl hydrocarbon chain, provided that the organic phase contains at least one solvent for the alkyl-ether polysaccharide.
2. Claim 1 wherein the polysaccharide has 2 to 4 hydroxyl groups substituted by saturated alkyl hydrocarbon chain.
3. Composition of any of the previous claims, wherein the saturated alkyl hydrocarbon chain contains 1 to 24 carbon atoms.
4. Composition of any of the previous claims, wherein the saturated alkyl hydrocarbon chain contains 2 to 10 carbon atoms.
5. Composition of any of the previous claims, wherein the saturated alkyl hydrocarbon chain is one of the following radicals: methyl, ethyl, n-propyl, i-propyl, n-butyl, i-butyl, t-butyl.
6. Composition of any of the previous claims, wherein the osidic rings are preferably selected from mannose, galactose, glucose, furanose, rhamnose and arabinose.
7. Composition of any of the previous claims, wherein alkyl-ether polysaccharides are alkyl-ether of a gum such as: guar gum, carob gum, karaya gum, tragacanth gum, or a mixture thereof.
8. Composition of any of the previous claims, wherein alkyl-ether polysaccharide is alkyl galactomannan with the alkyl chain of C<sub>1</sub> to C<sub>6</sub>, particularly C<sub>1</sub> to C<sub>3</sub>.
9. Composition of any of the previous claims, wherein the alkyl-ether polysaccharide is guar gum with a degree of substitution of 2 to 3.
10. Composition of any of the previous claims, wherein the alkyl-ether polysaccharide has a M<sub>w</sub> greater than 200,000.
11. Composition of any of the previous claims, wherein the weight ratio of the amount of oil phase to alkyl-ether polysaccharide can go from 5 to 500.
12. Composition of any of the previous claims, wherein alkyl-ether polysaccharide concentration (by weight) can go from 0.2 to 20%, particularly, from 1.5 to 8%.
13. Composition of any of the previous claims, wherein the film-forming polymer is one of the following: nitrocellulose, acetobutyrate cellulose, butyralpolyvinyl, resins resulting from condensation of formaldehyde with arylsulfonamide, alkyde resins, polyesters, acrylics, polyurethanes.
14. Composition of any of the previous claims, wherein film-forming polymer concentration (by weight) can go from 0.5 to 40%.
15. Composition of any of the previous claims, wherein the above-mentioned solvent is an organic solvent.
16. Composition of any of the claims 1 thru 14, wherein the above-mentioned solvent is an oil.
17. Composition of any of the previous claims, that include at least a complementary oil that is not a solvent for the alkyl-ether polysaccharide.
18. Composition of any of the previous claims, that include at least a plasticizer for the film-forming polymer.
19. Composition of any of the previous claims, that include at least a pyrogenic silica compound.
20. Claim 19 where pyrogenic silica concentration (by weight) can go from 0.1 to 5%, preferably from 0.5 to 1%.
21. Composition of any of the previous claims, that include at least a clay product as a complementary product.



22. Claim 21 where clay concentration (by weight) can go from 0.1 to 3%, preferably from 0.5 to 1.5%.
23. Composition of a nail treatment product or nail polish containing a film-forming polymer and an organic phase that contains an alkyl-ether polysaccharide defined by claim 1 to 10, and a solvent for the above-mentioned alkyl-ether polysaccharide.
24. Usage of the alkyl-ether polysaccharide (formed from units comprising at least two different osidic rings, each unit having at least one hydroxyl group substituted by a saturated alkyl hydrocarbon chain), as a thicken agent in a composition that includes a film-former polymer and an organic phase that contains at least a solvent for the above mentioned alkyl-ether polysaccharide.
25. Claim 24 wherein the alkyl-ether polysaccharide is one of the following gums: guar gum, carob gum, karaya gum, tragacanth gum, or a mixture thereof.
26. Formulations of cosmetic products for the treatment and care of keratinic material, obtained from any of the claims 1 to 22.
27. Formulation of a make-up product obtained from any of the claims 1 to 22.